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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to the Surface Treatment of Aluminium or Aluminium Alloys.

I, ROBERT SECREST DUNHAM, a citizen of the United States of America, of 118, Riverside Drive, City and State of New York, United States of America, Assignee of MARTIN TOSTERUD, of 1807, Ridge Avenue, Arnold, Pennsylvania, United States of America, a citizen of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the treatment of aluminium and aluminium alloy surfaces to produce thereon colored coatings, the chief object being to provide colored coatings of substantially any hue, which are uniform and of a permanent character. The term "aluminium" as used herein and in the appended claims includes that metal in every degree of purity and all alloys thereof containing a sufficient aluminium to permit the formation of a suitable oxide coating on the surface of the article, as explained hereinafter, that is to say, alloys in which the aluminium-content is 50 per cent., approximately, or more.

It is very often desirable to durably color metal surfaces. Aluminium and aluminium alloys have been the subject of numerous investigations directed toward the development of colored coatings on the metal surface, and attempts have been made to develop, chemically, coatings on aluminium and its alloys which are resistant to corrosion.

In experiments directed toward the development of a method of coloring aluminium, it has been discovered that if certain oxide coatings are anodically produced on aluminium or aluminium alloys and the coated metal then submitted to a dyeing operation, certain dyes such as anthracene blue, anthraquinone blue and alizerine red S, will be adsorbed in the coating thus imparting to the metal the characteristic color of the dye material used.

It has been the previous experience, however, that not all organic compounds of the class generally known as dyes and used as coloring mediums will produce the desired results and that when the coated metal is treated with a solution of a basic organic dye the dye is not selectively adsorbed in the coating and the metal is not, therefore, colored. Because of the brilliant and characteristic colors of the basic organic dyes it is desirable that a method be provided by which they may be utilized for the coloring of aluminium or its alloys.

The term "basic organic dye" is used herein and in the appended claims with the significance and meaning attached thereto by the coloring art. The term denotes dyes which are the salts of organic bases (which bases in the free state are colorless and insoluble), the name of the dyes being derived from the fact that their dyeing power resides entirely in the basic part of the salt.

According to this invention a basic organic dye is mordanted in the adsorbent oxide coating of an aluminium or aluminium alloy article. The aluminium or aluminium alloy articles provided with a suitable oxide coating are immersed in a solution of a mordant and are thereafter immersed in a solution of a basic organic dye, the dye will be readily adsorbed in the mordant-containing oxide coating to produce on the oxide-coated aluminium or aluminium alloy a uniformly colored surface of pleasing appearance.

The term "oxide coating" as used herein and in the appended claims is a well known designation of the art which describes a layer of aluminium oxide artificially produced on the aluminium or aluminium alloy surfaces by treatment of the metal surfaces with acids, preferably sulfuric or chromic, or with alkalies, such as sodium carbonate or the alkali sulfates and acid sulfates, for example sodium sulfate or sodium acid sulfate, all with or without the addition of other substances and with or without the use of externally-applied electrical energy. The term "oxide coating" does not include the very thin film of aluminium oxide which is naturally formed upon the metal by contact with the air.

In practicing the invention in the preferred manner, the aluminium or alu-

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minium alloy which is to be treated is first provided with an oxide coating of certain characteristics. In order that the coating will not later separate from the metal surface, it is necessary that it be hard, dense, and adherent. Of great importance, however, is the adsorbent nature of the coating. In order to obtain the most satisfactory results, the oxide coating should be adapted to adsorb a substantial amount of the solution with which, as above mentioned, it later comes in contact.

To produce adsorbent oxide coatings of a nature suitable to the purpose of the invention, a large number of solutions have been used, among which are included solutions of sulfuric acid, chromic acid, sodium carbonate with potassium dichromate, phosphoric acid and the salts thereof, ammonium citrate or lactate, citric acid and the salts thereof, and sodium carbonate. The treatment of the aluminium or aluminium alloy with these solutions to produce the desired oxide coating may consist in either immersing the metal in the solution and allowing the coating to be formed by the action of the solution, or by supplementing the action of the solution by making the metal to be coated the anode of a cell in which the solution serves as the electrolyte, and then impressing external electrical energy upon the electrodes of the cell. The manner and detail of forming oxide coatings on aluminium and aluminium alloys by means of the solutions and methods above mentioned are well known and sufficiently described in the art, and consequently only the preferred solutions and methods will be specifically described. The solutions which it is preferred to use in the preparation of an oxide-coated aluminium or aluminium alloy article are two, viz: sulfuric acid, or sodium carbonate and potassium dichromate. In forming an oxide coating on aluminium or its alloys by the use of solutions of sulfuric acid, aqueous solutions are preferably used, the concentration of the acid ranging from about 1 to 75 per cent. The metal article to be coated is placed in the bath and made the anode of an electric circuit of which another aluminium object or lead or other metal may be the cathode. When a solution of 7 per cent sulfuric acid is used, a current of from about 0.01 to 0.4 amperes per square inch of anode surface is impressed upon the circuit and the action on the aluminium or aluminium alloy is allowed to continue for about thirty minutes. When lower concentrations of acid are used, heating of the solution is preferred to increase the rapidity of action. With high concentrations of acid, lower current densities are preferably impressed on the anode.

When a solution of sodium carbonate and potassium dichromate is used to produce an oxide coating on aluminium or aluminium alloys, it is found preferable to simply immerse the piece to be coated in the solution without applying any external electrical energy. It is also preferred to heat the solution to boiling during the coating process. A solution containing about 0.5 to 6 per cent. of sodium carbonate and about 0.1 to 1 per cent. of potassium dichromate will give good results, but as a specific solution, one containing about 2 per cent. of sodium carbonate and 0.5 per cent. of potassium dichromate is preferred.

After the oxide-coated aluminium or aluminium alloy has been prepared in the above manner, the coated metal is ready to be treated by the methods of the invention which comprises, as hereinabove mentioned, as the first step the treatment of the coated metal in a mordant solution, during which treatment the mordant solution is adsorbed in the oxide coating, and as a second step a further treatment of the oxide-coated metal in or with a solution of a basic organic dye. The surface of the oxide-coated metal is thus, in accordance with the invention, brilliantly colored and the basic organic dye so firmly and adherently adsorbed in the oxide coating as to substantially become for all practical purposes, an integral and permanent part thereof.

In the step which involves the treatment of the oxide-coated metal with a solution of a mordant, there may be used as a mordant any substance which will, when adsorbed in the oxide coating, cause the adsorption therein and adherence thereto of the basic organic dye with which the oxide-coated metal is thereafter to be treated. The term "mordant" is used herein and in the appended claims in the ordinary significance and meaning with which it is used in the coloring or dyeing art. Among the many substances which may be used as mordants are tannic acid, citric acid, tartaric acid, phospho-tungstic acid, salicylic acid, oxalic acid, stearic acid, sulphonated castor oil, benzoic acid sodium silicate, cream of tartar, ammonium oxalate, sodium benzoate, ferric ammonium citrate, di-ammonium hydrogen phosphate, sodium oxalate, di-sodium hydrogen phosphate, sodium tartrate, ammonium citrate, sodium borate, ammonium molybdate, ammonium citrate, pyrogallic acid, antimony potassium tartrate, potassium ferrocyanide, sodium benzoate, and potassium dichromate.

In the next step in the preferred practice of the invention, the oxide-coated metal, the coating of which carries an adsorbed mordant, is treated in any convenient way with a solution of basic organic dye of the characteristic color desired. This treatment, which may be effected by simple immersion or spraying, imparts to the surface of the metal the color of the dye, after which the article is dried in any convenient manner.

In the practice of the invention, any of the basic organic dyes may be used, among which Safranine T, Rhodamine B, Victoria Green, Auramine, Chrysoidine R, Brilliant Green B and Victoria Blue B may be named. The invention is not, however, limited to those specifically mentioned but includes all basic organic dyes as herein defined.

In practicing the steps of the novel process, it has been determined that the concentration of the solutions in which the oxide-coated metal is immersed is not a critical factor and that solutions containing as little as 1 per cent. by weight of the soluble compounds used, or solutions which are completely saturated with the soluble compounds, will produce the colors desired, but the latter have been found more advantageous in general. It has been further determined that the temperature of the solutions at the time at which the oxide-coated metal is introduced therein is not a governing factor and that satisfactory colors may be produced whether the solution be hot or cold.

As specific examples of the product of the invention, the following may be cited:

EXAMPLE A.

An aluminium alloy article was provided with a suitable oxide coating by making the article the anode of an electrolytic cell in which an aqueous solution of sulfuric acid was used as the electrolyte. The resulting oxide-coated article was washed and thereafter immersed in a 5 per cent. aqueous solution of potassium antimony tartrate for about 10 minutes. The article was then thoroughly washed and a brilliant red color was produced therein by immersing the article for about 12 minutes in a 1 per cent. aqueous solution of Safranine T.

EXAMPLE B.

An aluminium article, provided with an oxide coating as in Example A, was immersed in a 3 per cent. aqueous solution of sodium silicate for about 10 minutes. The article was then thoroughly washed and a deep blue color produced thereon by immersing the washed article for about 15 minutes in a 1 per cent. solution of Victoria Blue B.

EXAMPLE C.

An aluminium article, provided with an oxide coating as in Example A, was immersed in a 5 per cent. aqueous solution of tannic acid for about 5 minutes. The article was then thoroughly washed and a brilliant red color produced thereon by immersing the washed article for about 10 minutes in a 1 per cent. aqueous solution of Rhodamine B.

EXAMPLE D.

The oxide-coated aluminium alloy article was immersed in a 5 per cent. solution of phospho-tungstic acid for about 15 minutes. The article was then thoroughly washed and a brilliant red coloring was produced on the article surface by immersing it for about 15 minutes in a 1 per cent. aqueous solution of Safranine T.

It is to be understood that the invention is not limited to the specific details herein described but may be carried out in other ways without departure from the broad aspects of the invention hereinafter claimed.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:—

1. A colored article of aluminium or aluminium alloy having an adsorbent oxide coating which is colored by a mordanted basic organic dyeing compound.

2. A colored article of aluminium or aluminium alloy having an adsorbent oxide coating in which is deposited a mordanted basic organic dye.

3. A colored article of aluminium or aluminium alloy having an adsorbent oxide coating which contains as an integral or permanent part thereof a coloring compound comprising a mordanted basic organic dye.

4. A method of coloring aluminium or aluminium alloy which comprises forming on the metal surface an adsorbent oxide coating, and thereafter mordanting in said coating a basic organic dye.

5. An impregnation method of coloring a pre-formed adsorbent oxide-coated surface of aluminium or aluminium alloy comprising mordanting in said coated surface a basic organic dye.

6. A method of coloring adsorbent oxide-coated aluminium or aluminium alloy surfaces, comprising treating the said surfaces successively with solutions of a mordant and of a basic organic dye capable of uniting with said mordant to produce in said surfaces an insoluble basic organic coloring compound.

7. A method of coloring adsorbent oxide-coated aluminium or aluminium alloy surfaces comprising immersing the

said oxide-coated metal in a mordanting solution to cause the adsorbent coating to adsorb a part of said solution and thereafter applying to said coating a basic organic dye capable of combining with said mordanting solution to produce a precipitate of characteristic color in situ.

8. A method of coloring aluminium or aluminium alloys substantially as herein before described.

9. A colored article of aluminium or aluminium alloy whenever colored by the processes hereinbefore described.

Dated the 17th day of December, 1931.

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